Kinetic modeling of homogeneous catalytic processes

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Abstract

Homogeneous catalysis by soluble metal complexes is gaining considerable attention due to their unique applications and features like high activity and selectivity. In this paper, a brief review of kinetic modeling in homogeneous catalysis has been presented. Approaches using empirical as well as molecular level rate models have been discussed. Special features relevant to asymmetric catalysis and multiple rate controlling steps have also been addressed. A case study on kinetics of carbonylation of 1-(4-*iso*-butylphenyl)ethanol using a homogeneous palladium catalyst has been discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Homogeneous catalysis; Kinetics; Rate equation; Hydrogenation; Hydroformylation; Carbonylation; 1-(4-*iso*-Butylphenyl)ethanol; Ibuprofen

1. Introduction

Kinetic modeling of catalytic reactions is one of the key aspects investigated in order to understand the rate behavior of catalytic reactions [1–10] as well as reaction mechanism [5–7]. A knowledge of intrinsic reaction kinetics (a scale independent property) and development of rate equations is most essential as a part of reaction engineering studies aimed to evolve strategy for reactor design. While, the subject of kinetic modeling has been well investigated for heterogeneous catalysis [8–10], only limited information is available on this aspect in homogeneous catalysis [1–7].

Homogeneous catalysts consisting of soluble transition metal complexes have several important applications in chemical industry for both bulk commodity as well as specialty products [11–15]. Some important examples are listed in Table 1. The newly emerging applications in fine chemicals and pharmaceuticals are particularly promising due to increased competition along with a need for selective, efficient and environmentally acceptable processes. Another important feature is their high selectivity for the synthesis of biologically active molecules with asymmetric centers [16]. Since, most of the new drug molecules are expected to be optically active isomers, homogeneous catalysis has a bright future in pharmaceutical industry. Homogeneous catalysis has so far been investigated with the perspective of reaction mechanism, in which the role of catalysts, ligands, co-catalysts and nature of catalytically active species have been studied [11–15]. While, a number of examples illustrate systematic studies of in situ spectroscopic analysis of catalytic reaction intermediates leading to description of catalytic cycles on a molecular level [17–19], correlation of these with kinetic data and development of rate equations has received limited attention. In this paper, the current state of development on kinetic modeling in homogeneous catalysis has been presented with a specific case study on kinetics of carbonylation of

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| **Nomenclature** |
| |
| B_1 concentration of IBPE in the liquid |
| phase at time t |
| B_0 initial concentration of IBPE in |
| the liquid phase |
| D_1 concentration of IBS in the liquid |
| phase at time t |
| E_1 concentration of IBPCl in the liquid |
| phase at time t |
| k_i rate constants |
| k_{-1}^{min} mac dissociation rate constant for the |
| minor diastereomer |
| k_1^{maj} mac binding rate constant for the |
| major diastereomer |
| k_1^{min} mac binding rate constant for |
| the minor diastereomer |
| k_2^{maj} rate constant for the H_2 addition |
| step for the major diastereomer |
| k_2^{min} rate constant for the H_2 addition |
| step for the minor diastereomer |
| K_i equilibrium or empirical constants |
| K_1^{maj} mac binding equilibrium constant |
| for the major diastereomer |
| K_1^{min} mac binding equilibrium constant |
| for the minor diastereomer |
| m, n, p reaction orders as given in Eq. (6) |
| P_{CO} partial pressure of CO |
| $P_{C_2H_4}$ partial pressure of C_2H_4 |
| P_1 concentration of carbonylated |
| products (IBN + IPPA) in the |
| liquid phase at time t |
| r_i rate of the reaction |
| r_{iso} rate of formation of the *iso*-isomer |
| r_n rate of formation of the *n*-isomer |
| $r_{R\text{-product}}$ rate of formation of the *R*-product |
| $r_{S\text{-product}}$ rate of formation of the *S*-product |
| $[X]$ concentration of the species X |
+---+

1-(4-*iso*-butylphenyl)ethanol (IBPE) using homogeneous Pd complex catalyst.

2. Kinetic models in homogeneous catalysis

As a first step in kinetic modeling, it is important to consider the reaction pathways and catalytic reaction mechanism for any given system. The mechanism of homogeneous catalytic reactions is complex even if only a single reaction is involved, since the catalytic cycle consists of several stoichiometric reactions. When a co-catalyst or a promoter is used, additional steps are associated with the catalytic cycle either to form the active catalytic species around which the principal catalytic cycle operates or to form an active substrate. The reactions may also involve one or more gas phase reactants or biphasic systems with catalyst and reactants/products present in different phases. These multi-phase catalytic gas–liquid reactions need consideration of interphase mass transfer steps in addition to the overall catalytic reactions. Thus, homogeneous catalytic reactions can be categorized as follows:

1. Single or multi-step reactions with only one catalytic component: the examples of this class are found in hydrogenation of olefins using RhCl-$(PPh_3)_3$, hydroformylation of olefins using $HRh(CO)(PPh_3)_3$, oligomerization of ethylene using Ni complex catalyst, etc.

2. Single or multi-step reactions with multi-component catalyst systems (catalyst/co-catalyst/promoter): the examples of this category include the Wacker process for oxidation of ethylene to acetaldehyde using $PdCl_2/CuCl_2$ and molecular oxygen. During conversion of ethylene to acetaldehyde, Pd^{2+} is reduced to Pd^0 and the co-catalyst $CuCl_2$ has a role to re-oxidize Pd^0 to the active Pd^{2+} [20]. Also the molecular oxygen has a role to re-oxidize the reduced co-catalyst and hence is only indirectly involved in catalysis. The re-oxidation is required to be faster than main oxidation reaction for the catalytic cycle to operate efficiently. Another important example is the carbonylation of methanol to acetic acid using Rh complex with HI as a promoter. In this case, the promoter HI converts the substrate methanol to CH_3I, an active substrate for carbonylation and the catalytic reaction proceeds only when Rh complex with HI promoter is used. Several examples with even more complex catalysis are known in homogeneous catalysis, a common feature in which the overall reaction is catalytic with regeneration of principle catalyst, co-catalyst as well as the promoter (as applicable).

3. Reactions involving two or more gas phase reactants with catalyst in solution with one or

Table 1
Applications of homogeneous catalysis in industry [11–15]

No.	Process	Catalyst	Company
1	Oxidation of ethylene to acetaldehyde	$PdCl_2/CuCl_2$	Wacker–Werke
2	Hydrocyanation of butadiene to adipic acid	Ni complex	Du Pont
3	Asymmetric hydrogenation of acetamido cinnamic acid (3-methoxy-4-acetoxy derivative) (l-dopa process)	$[Rh(diene)(solvent)]^+/dipamp$	Monsanto
4	Hydroformylation of propene to butyraldehyde	$NaCo(CO)_4$	BASF
		$HCo(CO)_3PBu_3$	Shell
		$HRh(CO)(PPh_3)_3$	Union Carbide
		Rh/TPPTS	Ruhrchemie–Rhone–Poulenc
5	Hydroformylation of diacetoxybutene to 1-methyl-4-acetoxy butanal (vitamin A intermediate)	$HRh(CO)(PPh_3)_3$	Hoffmann–La Roche
		Rh catalyst	BASF
6	Carbonylation of methanol to acetic acid	Rh/iodide	Monsanto
		$Co_2(CO)_8$	BASF
		Ir/iodide	BP Chemicals
7	Carbonylation of methyl acetate to acetic anhydride	Rh/MeI	Halcon
		Rh/MeI	Eastman Chemical
8	Carbonylation of ethylene to propionic acid	$Ni(OCOC_2H_5)_2$	BASF
9	Carbonylation of butadiene to adipic acid	$Co_2(CO)_8/pyridine$	BASF
10	Carbonylation of IBPE to ibuprofen	$PdCl_2(PPh_3)_2/HCl$	Hoechst–Celanese
11	Carbonylation of propyne to MMA	$Pd(OAc)_2/2\text{-PyPPh}_2$	Shell
12	Oxidative carbonylation of methanol to dimethyl carbonate	$PdCl_2–CuCl_2$	Assoreni
13	Co-polymerization of CO and ethylene to polyketones	$Pd(OAc)_2/dppp/TsOH$	Shell
14	Amidocarbonylation of benzaldehyde to phenylglycene	$PdBr_2(PPh_3)_2$	
15	Hydroaminomethylation of olefins to primary amines	$[Rh(COD)Cl]_2$	
16	Heck arylation of ethylene with 2-bromo-6-methoxy naphthalene	Palladacycles	Hoechst AG

more catalyst components, the examples of which are found in hydroformylation, oxidative carbonylation and copolymerization, etc.

4. Biphasic reactions with or without gas phase reactants and catalyst being soluble in one of the phases, the examples of which are hydroformylation, carbonylation, hydrogenation, etc. using water soluble metal complex catalysts and phase transfer catalytic reactions.

Due to the various complexities involved as indicated in the examples shown above, the kinetics of such reactions are often represented by non-linear rate equations, some purely empirical and some derived based on a mechanism. A summary of kinetic studies in homogeneous catalysis is presented in Table 2. It can be noted that the mathematical forms of rate equations used range from simple power law types to hyperbolic forms to those derived based on mechanisms already established. In some cases, a close analogy to the rate equations used in heterogeneous catalysis

(e.g. based on Langmuir–Hinshelwood mechanism) is observed except that in homogeneous catalysis the mechanisms considered involve molecular level description of the catalytic intermediate species. For some cases, like hydroformylation, even though the catalytic cycle is reasonably well established, the rate equations used are empirical due to complexities such as substrate inhibition with CO and also olefins. However, it would be more appropriate to develop rate equations based on a molecular level and correlate the observed trends with the mechanism. Salient features of the kinetic studies for a few examples are discussed below.

Hydrogenation of olefins using homogeneous catalysis is an excellent example to illustrate the molecular level approach to kinetic modeling as the mechanism of these reactions has been well established. Osborn et al. [21] studied kinetics of hydrogenation of cyclohexene using $RhCl(PPh_3)_3$ catalyst and proposed a rate equation assuming a reaction mechanism in which parallel steps to activate olefins and hydrogen are

Table 2
A summary of kinetic studies in homogenous catalysis

No.	Reaction	Catalyst	Rate equation
1	Carbonylation of methanol	$RhCl_3$/HI	$r = k$[Rh][CH_3I], zero order with CO and methanol
		$RhCl_3$/HI [25]	$r = \dfrac{k[\text{catalyst}]_t[\text{I}]_t[\text{MeOH}]}{[\text{water}] + K_1[\text{CH}_3\text{OH}]_t + K_2[\text{I}]_t[\text{CH}_3\text{COOH}]}$
		$NiCl_2$/iso-quinoline [26]	$r = \dfrac{k[\text{CO}][\text{substrate}]}{(1 + K_1[\text{CO}])(1 + K_2[\text{substrate}])(1 + K_3[\text{water}])^2}$
2	Carbonylation of styrene	$PdCl_2(PPh_3)_2$ [27–32]	See Eqs. (7)–(10)
		$Pd(OAc)_2$/PPh_3/TsOH [33]	$r = \dfrac{kP_{\text{CO}}(1 + K_1[\text{styrene}])^2[\text{catalyst}][\text{water}]}{(1 + K_2 P_{\text{CO}})(1 + K_3[\text{water}])^2}$
3	Hydrogenation of cyclohexene	$RhCl(PPh_3)_2$ [21]	$r = \dfrac{kK_1[\text{H}_2][\text{substrate}][\text{catalyst}]}{1 + K_1[\text{H}_2] + K_2[\text{substrate}]}$
4	Hydrogenation of allyl alcohol	$RhCl(PPh_3)_3$ [22]	$r = \dfrac{kK_1[\text{H}_2][\text{substrate}][\text{catalyst}]}{1 + K_1[\text{substrate}] + K_1 K_2[\text{substrate}]^2 + [\text{PPh}_3]/K_3}$
5	Asymmetric hydrogenation of mac	$[Rh(dipamp)S_2]^+$ [36]	See Eqs. (1)–(5)
6	Hydroformylation of propylene	$HCo(CO)_4$ [39]	$r = \dfrac{k[\text{substrate}][\text{catalyst}][\text{H}_2]}{[\text{CO}]}$
7	Hydroformylation of propylene	$Co_2(CO)_8$ [40]	$r_n = \dfrac{k[\text{H}_2]^{0.55}[\text{CO}][\text{catalyst}]^{0.75}[\text{substrate}]^{0.87}}{(1 + K_1[\text{CO}])^2}$
			$r_{iso} = \dfrac{k[\text{H}_2]^{0.32}[\text{CO}][\text{catalyst}]^{0.62}[\text{substrate}]}{(1 + K_2[\text{CO}])^2}$
8	Hydroformylation of 1-hexene, allyl alcohol, vinyl acetate	$HRhCO(PPh_3)_3$ [41–43]	See Eq. (6)
9	Hydroformylation of 1-decene, styrene	$HRhCO(PPh_3)_3$ [44]	See Eq. (7)
10	Hydroformylation of ethylene	$Rh(acac)(CO)_2$/PPh_3 [47]	$\text{TOF} = \dfrac{k_1(P_{\text{C}_2\text{H}_4}/[\text{PPh}_3])}{1 + K_1(P_{\text{CO}}/[\text{PPh}_3]) + K_2([\text{PPh}_3]/P_{\text{CO}})}$
11	Hydroformylation of 1-octene	$[RhCl(1,5\text{-COD})]_2$/TPPTS [51]	$r = \dfrac{k[\text{H}_2][\text{CO}][\text{catalyst}][\text{substrate}]}{(1 + K_1[\text{CO}])^2(1 + K_2[\text{H}_2])}$
12	Hydroformylation under supercritical CO_2	$HRh(CO)[p\text{-CF}_3\text{C}_6\text{H}_4)_3]_3$ [52]	$r = \dfrac{k[\text{H}_2]^{0.48}[\text{catalyst}]^{0.84}[\text{octene}]^{0.5}}{1 + K_1[\text{CO}]^{2.2}}$
13	Oxidation of cyclohexane	$Mn(OAc)_2$ [34]	$r = \dfrac{k[\text{substrate}][\text{catalyst}]}{K_1 + K_2[\text{catalyst}]}$
14	Heck coupling of iodobenzene and methyl acrylate	$Pd(OAc)_2$/PPh_3 [35]	$r = \dfrac{k[\text{PhI}][\text{olefin}]^2[\text{Me}_3\text{N}][\text{catalyst}]}{(1 + K_1[\text{olefin}]^2)(1 + K_2[\text{Me}_3\text{N}]^4)(1 + K_3[\text{catalyst}])^3} \times (1 + K_4[\text{PPh}_3])$

considered. Wadkar and Chaudhari [22] showed that for substrates like allyl alcohol, substrate inhibition is observed and proposed a rate equation with modified reaction mechanism. Similar studies on hydrogenation of cyclohexene, maleic acid, acrylamide and allyl alcohol using $RuCl_2(PPh_3)_3$ catalyst have also been reported and rate equations proposed [2,23,24].

A kinetic analysis of enantioselective hydrogenation of methyl-(Z)-α-acetamidocinnamate (mac) has been studied by Landis and Halpern [36] and rate equations

were proposed considering a molecular level mechanism to demonstrate the role of kinetics on enantioselectivity. Their kinetic studies showed that the predominant stereo isomer (*S*)-*N*-acetylphenylalanine methyl ester was derived from the minor less stable catalytic intermediate [Rh(dipamp)(mac)]$^+$ by virtue of its much higher reactivity towards H_2. The enantioselectivity was found to decrease with increase in H_2 pressure. The observed variation in enantioselectivity with H_2 pressure has been explained considering different rate-determining steps at lower and higher H_2 pressures. At lower H_2 pressures, oxidative addition of H_2 is the rate-determining step for both the isomers. With increasing H_2 pressure, oxidative addition of H_2 competes with the dissociation of substrate, mac. Since $k_2^{min} \gg k_2^{maj}$, such competition starts at a lower pressure for the minor diastereomer than for the major diastereomer. In this regime, the rate-determining step for major diastereomer is still the H_2 addition step, while rate of minor diastereomer pathway is given by a steady state rate equation. Thus, the rate corresponding to the major diastereomer pathway, which contributed only a small fraction of the total product remains first order in H_2 pressure and the rate of minor diastereomer pathway becomes independent of the H_2 pressure. Hence, as the H_2 pressure is increased, the total reaction rate is expected to level off and the enantioselectivity to decrease. At higher H_2 pressure, the oxidative addition step becomes faster than the substrate binding steps and the reaction rate and enantioselectivity are determined by the substrate (mac) association step and independent of H_2 concentration. The rate equations proposed for the three cases are:

Case 1. Oxidative addition of H_2 as the rate-determining step for both the stereo isomers:

$$r_{R\text{-product}} = \frac{k_2^{maj} K_1^{maj} [H_2][Rh]_{tot}}{K_1^{maj} + K_1^{min}} \tag{1}$$

$$r_{S\text{-product}} = \frac{k_2^{min} K_1^{min} [H_2][Rh]_{tot}}{K_1^{maj} + K_1^{min}} \tag{2}$$

Case 2. Oxidative addition of H_2 for *R*-isomer and a steady state rate equation for the *S*-isomer:

$$r_{R\text{-product}} = k_2^{maj}[Rh][H_2] \tag{3}$$

$$r_{S\text{-product}} = \frac{k_2^{min} k_1^{min} [Rh][H_2]}{K_1^{maj}(k_{-1}^{min} + k_2^{min}[H_2])} \tag{4}$$

Case 3. Association of substrate (mac) as the rate-determining step:

$$r = k_1^{maj}[Rh]_{tot}[mac] + k_1^{min}[Rh]_{tot}[mac] \tag{5}$$

Other important aspect of kinetics of asymmetric catalysis concerning non-linear effects [37] on enantioselectivity occurring due to the association of chiral ligands inside or outside the catalytic cycle and conversion dependent [38] enantioselectivity have also been addressed.

Kinetic modeling of hydroformylation of propylene and cyclohexene was studied by Natta et al. [39] using co-carbonyl catalyst. The reaction was found to be first order with olefin, catalyst and hydrogen but negative order dependent with CO. Gholap et al. [40] reported rate equations to represent kinetics of formation of both *n*- and *iso*-butyraldehyde in co-carbonyl catalyzed hydroformylation of propylene. Deshpande and Chaudhari [41–43] investigated detailed kinetics of hydroformylation of 1-hexene, allyl alcohol and vinyl acetate using HRh(CO)(PPh$_3$)$_3$ catalyst and proposed the following form of rate equations:

$$r = \frac{k[H_2]^m[CO][catalyst][substrate]}{(1 + K_1[substrate])^n (1 + K_2[CO])^p} \tag{6}$$

The important observations were a strong substrate inhibition with respect to CO and a mild substrate inhibition with respect to olefins and requirement of a critical catalyst concentration. However, in all these cases, the rate models proposed were empirical in spite of a reasonably well-understood mechanism for hydroformylation. In recent investigations, Divekar et al. [44] and Nair et al. [45] derived rate equations considering a molecular level approach based on the mechanism proposed by Evans et al. [46] for HRh(CO)(PPh$_3$)$_3$ catalyzed hydroformylation of 1-decene and styrene, respectively. The rate model derived assuming oxidative addition of hydrogen to Rh-acyl species as the rate-determining step was

$$r = \frac{kK_1 K_2 [H_2][CO][catalyst][substrate]}{1 + K_2[CO] + K_1 K_2[CO][substrate] + K_1 K_2 K_3[CO]^2[substrate] + K_1 K_2 K_3 K_4[CO]^3[substrate]} \tag{7}$$

This model predicted the negative order dependence with CO, a unique feature of kinetics of olefin hydro-

formylation. Kiss et al. [47] also reported a mechanistic model for kinetics of ethylene hydroformylation using $Rh(acac)(CO)_2/PPh_3$ catalyst with unusual observations of first order with ethylene at higher PPh_3 concentration and zero order at lower PPh_3 concentration. The complex kinetics and change in reaction orders have been explained as a result of shift in rate-determining step under different conditions.

Kinetics of biphasic hydroformylation of 1-octene [48], ethylene [49] and styrene using water soluble Rh–TPPTS [50] catalyst has also been studied and rate equations proposed. In contrast to the earlier reports using homogeneous catalysts, in this case, substrate inhibition with CO was not observed. This is due to the lower range of dissolved CO concentrations as a result of lower solubility in aqueous catalyst phase. The effect of co-solvent on kinetics of biphasic hydroformylation of 1-octene has been reported by Purwanto and Delmas [51] for a catalyst prepared from a precursor $[Rh(COD)Cl]_2$ and TPPTS ligand. Due to enhancement of solubility of CO in the presence of the co-solvent, ethanol, a substrate inhibition with CO was observed as expected.

In a recent study, Palo and Erkey [52] reported kinetics of hydroformylation of 1-octene in supercritical CO_2 with $HRh(CO)[p\text{-}CF_3C_6H_4)_3]_3$ as a catalyst at $50°C$ and 273 bar pressure. The reaction order was found to be 0.5 with H_2 and 1-octene, 0.84 with catalyst and a negative order with CO. The catalyst solubility in supercritical CO_2 is reported to be higher than that in organic solvents and the critical catalyst concentration was not observed like the conventional homogeneous catalysts [41–43]. The main advantage of supercritical CO_2 claimed is the higher solubility of H_2, CO and catalyst, but for hydroformylation, the higher CO concentration is not desirable due to rate inhibition with CO and hence it is necessary to optimize the H_2/CO ratio for achieving higher rates in supercritical medium.

Carbonylation of methanol using Rh, Ir and Ni complex catalysts has been studied by Roth et al. [53] as well as by Chaudhari and coworkers [26,54] and rate equations were proposed (see Table 2). The kinetics observed was indeed very simple for Rh/HI catalyst with a zero order with methanol and CO and first order with Rh and HI. This correlates with the mechanism assuming oxidative addition of CH_3I to Rh complex as the rate-determining step, which was validated independently by characterization of catalytic intermediates using in situ IR and NMR techniques [17]. A detailed review on the history of kinetics and mechanism of methanol carbonylation has been given by Maitlis [17], which is one of the best examples of kinetics and mechanism investigated with excellent correlation of observed kinetics with mechanism.

Another important example of kinetic modeling in homogeneous catalysis is the carbonylation of styrene using $Pd(OAc)_2/PPh_3/TsOH$ in methanol [33] wherein an empirical rate equation was found suitable to explain the kinetic trends. The rate of carbonylation varied linearly with catalyst and was zero order with respect to styrene up to a certain concentration beyond which an unusual trend of increase in reaction rate was observed. Water also showed a remarkable promoting effect on reaction rate up to a certain concentration.

Similarly, a detailed kinetic analysis of hydrocarboxylation of styrene to 2- and 3-phenyl propionic acids has been reported by Noskov and coworkers [27–32] using $PdCl_2(PPh_3)_2$ as a catalyst. Kinetic rate models were developed to explain the effect of different parameters on the rates of formation of *iso* as well as linear acids, which determine the regioselectivity. The following rate equations were proposed which explained the combined effects of P_{CO} and H_2O on the formation of individual isomers based on a molecular approach:

$$r_n = \frac{[H_2O][Pd]_0}{1 + K_1[H_2O]^2 P_{CO}/[HCl] + K_2[H_2O]^2} \times \left[K_3 + \frac{K_4 P_{CO}}{1 + K_5 P_{CO}} \right] \tag{8}$$

$$r_{iso} = \frac{[H_2O] P_{CO}{}^2 [Pd]_0}{1 + K_1[H_2O]^2 P_{CO}/[HCl] + K_2[H_2O]^2} \times \left[\frac{K_4 K_5}{1 + K_5 P_{CO}} + \frac{K_6[H_2O]}{([HCl] + K_7[H_2O])} \times (1 + K_8[H_2O]) \right] \tag{9}$$

where K_i are the constants and P_{CO} is the effective CO pressure. Other parameters, which affected the *n/iso* ratio, were the concentrations of styrene and PPh_3. The rate of formation of *n*-isomer was zero order with respect to styrene and more than zero in the case of *iso*-isomer. An increase in concentration of

PPh$_3$ decreased rate of formation of the *iso*-isomer to a greater extent than that of *n*-isomer. The above rate equations (Eqs. (8) and (9)) were modified (Eqs. (10) and (11)) to explain these effects.

$$r_n = \frac{[H_2O][Pd]_0}{1 + K_1[H_2O]^2 P_{CO}/[HCl] + K_2[PPh_3][H_2O]^2}$$
$$\times \left[K_3 + \frac{K_4 P_{CO}}{1 + K_5 P_{CO}} \right] \qquad (10)$$

$$r_{iso} = \frac{[H_2O] P_{CO}{}^2 [Pd]_0}{1 + K_1[H_2O]^2 P_{CO}/[HCl] + K_2[PPh_3][H_2O]^2}$$
$$\times \left[\frac{K_4 K_5}{1 + K_5 P_{CO}} + \frac{K_6[H_2O][styrene]}{([HCl] + K_7[PPh_3][H_2O])} \atop \times ([styrene] + K_8[H_2O]) \right] \qquad (11)$$

Liquid phase oxidation is an important class of homogeneous catalytic reactions and a review of kinetic modeling of such systems has been presented by Mills and Chaudhari [55]. In some cases, oxidation involves redox mechanism in which re-oxidation is required to be faster than other steps in the catalytic cycle. Thus, a critical oxygen/oxidant concentration exists below which the catalytic cycle will fail to operate. A detailed analysis of this aspect has been given by Bhattacharya and Chaudhari [56] for the Wacker process.

3. Carbonylation of IBPE using PdCl$_2$(PPh$_3$)$_2$/TsOH/LiCl catalyst

Carbonylation of IBPE represents an example of a homogeneous catalytic reaction involving single reaction but three catalyst components. As a result, the reaction mechanism and catalytic cycle also involve series of elementary reaction steps. Kinetic modeling of this industrially important reaction [57–59] has been presented here as a detailed case study. The reaction involves three important steps: (i) formation of the active substrate 1-(4-*iso*-butylphenyl)ethyl chloride (IBPCl) through 4-*iso*-butylstyrene (IBS) as an intermediate, (ii) conversion of PdCl$_2$(PPh$_3$)$_2$ to the active Pd(0) species, and (iii) catalytic carbonylation of IBPCl (the main catalytic cycle) as shown in Fig. 1.

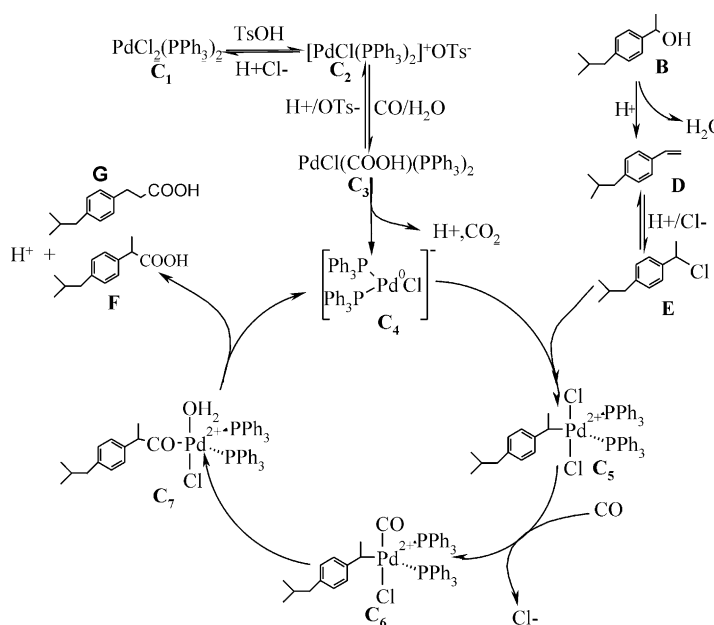Several experiments were carried out in which concentration–time profiles were observed at

Fig. 1. Proposed mechanistic pathway for carbonylation of IBPE (**B**).

different concentrations of IBPE, water, $PdCl_2(PPh_3)_2$, TsOH/LiCl, CO pressure and temperatures. The average rate of carbonylation was found to vary with first order dependence with concentration of water, of the order 0.8 with CO, 0.7 with IBPE and 0.43 with respect to catalyst concentration. Even though the empirical rate model predicted [60] the concentration–time data well for certain conditions, a more appropriate method would be that considering a molecular level approach. Since, the average rate of carbonylation shows dependence on several parameters, deriving a rate model assuming any one of the steps as rate-determining step would not explain all the observed trends. In this case, a dynamic analysis incorporating the variation of concentrations of all the catalytic species as well as reaction intermediates with time would be most suitable as it would allow consideration of more than one step as rate limiting. An attempt has been made to interpret the concentration–time data for carbonylation of IBPE using a dynamic approach for one specific case as demonstrated below.

The rate of change of concentration of IBPE (**B**), IBS (**D**), IBPCl (**E**) and the carbonylation products (**F**+**G**) as well as the catalytic intermediates (as shown in Fig. 1) with time in a semi-batch reactor can be represented as follows:

$$-\frac{dB_1}{dt} = r_1 = k_1[B_1][H^+] \tag{12}$$

$$\frac{dD_1}{dt} = r_1 - r_2 + r_3 = k_1[B_1][H^+]$$
$$-k_2[D_1][H^+][Cl^-] + k_3[E_1][H^+] \tag{13}$$

$$\frac{dE_1}{dt} = r_2 - r_3 - r_4 = k_2[D_1][H^+][Cl^-]$$
$$-k_3[E_1][H^+] - k_4[E_1][C_4] \tag{14}$$

$$-\frac{dC_1}{dt} = r_6 = k_5[C_1][CO][H_2O] \tag{15}$$

$$\frac{dC_4}{dt} = r_5 - r_4 + r_7 = k_5[C_1][CO][H_2O]$$
$$-k_4[E_1][C_4] + k_7[C_7][H_2O] \tag{16}$$

$$\frac{dC_5}{dt} = r_4 - r_6 = k_4[E_1][C_4] - k_6[C_5][CO] \tag{17}$$

$$\frac{dC_7}{dt} = r_6 - r_7 = k_6[C_5][CO] - k_7C_7[H_2O] \tag{18}$$

$$\frac{dP_1}{dt} = r_7 = k_7C_7[H_2O] \tag{19}$$

with initial conditions

at $t = 0$, $B_1 = B_0$, $D_1 = E_1 = P_1 = 0$,
$C_1 = C_0$ and $C_4 = C_5 = C_7 = 0$ (20)

where k_1, k_2, k_3, k_4, k_5, k_6 and k_7 represent the rate constants, B_0 the initial concentration of IBPE, B_1, D_1, E_1 and P_1 the concentrations of IBPE, IBS, IBPCl and total amount of carbonylated products [2-(4-iso-butylphenyl)propionic acid (IBN)+3-(4-iso-butylphenyl)propionic acid (3-IPPA)], respectively, C_0 the initial concentration of the catalyst, and C_1, C_4, C_5, and C_7 the concentrations of various catalytic species as shown in Fig. 1.

The differential equations (12)–(19) were solved by using the initial conditions (Eq. (20)) and guess values for the rate parameters using a fourth order Runge–Kutta method. A comparison of the experimental and predicted concentration–time data for a standard experiment using the dynamic model is shown in Fig. 2.

The values of rate constants determined for a set of conditions given in Fig. 2 are: $k_1 = 0.00745\,(m^3/kmol)^2\,s^{-1}$, $k_2 = 0.0125\,(m^3/kmol)^2\,s^{-1}$, $k_3 =$
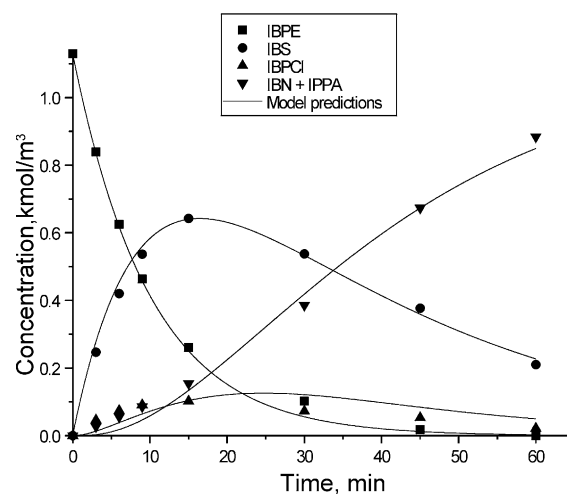

Fig. 2. Comparison of experimental and predicted concentration–time profiles using the dynamic model. Reaction conditions: IBPE, 1.123 kmol/m³; TsOH/LiCl (1:1), 0.121 kmol/m³; P_{CO}, 5.4 MPa; $PdCl_2(PPh_3)_2$, 1.121 × 10⁻³ kmol/m³; PPh₃, 2.242 × 10⁻³ kmol/m³; water, 2.67 kmol/m³; MEK, 1.95 × 10⁻⁵ m³; T, 388 K.

$0.0016\,\mathrm{m^3/kmol\,s^{-1}}$, $k_4 = 1.5939\,\mathrm{m^3/kmol\,s^{-1}}$, $k_5 = 0.150\,\mathrm{(m^3/kmol)^2\,s^{-1}}$, $k_6 = 0.2139\,\mathrm{m^3/kmol^2\,s^{-1}}$, and $k_7 = 0.952\,\mathrm{m^3/kmol\,s^{-1}}$. In addition to the prediction of the concentrations of the reaction intermediates, the dynamic model can also be used for the prediction of the change of concentrations of different catalytic intermediates with time. Considering the complexities involved in the dynamic model, a more rigorous analysis is required which needs a robust numerical/optimization technique. However, this approach will be more useful in understanding the dynamic changes in the concentration of catalytic species and the kinetics and mechanism in a molecular level.

4. Conclusions

Kinetic modeling of homogeneous catalytic reactions has been reviewed, which indicated that two types of rate models consisting of empirical as well as those derived based on a mechanism involving well-defined catalytic species have been used. Most of these models assume one step as rate controlling, which may not be true in many cases. Rigorous methodologies for the analysis of reactions with multiple rate controlling steps, parameter estimation for complex rate forms and criteria for discrimination of rate models need to be developed. Special cases like non-linear effects in asymmetric catalysis, complexities of phase equilibrium and supercritical medium on kinetics also will require further work. Attempt should also be made to achieve correlations between the kinetic models, catalytic cycles and the in situ spectroscopic studies of catalytic species.

Acknowledgements

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